NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3281

INTERGRANULAR CORROSION OF HIGH-PURITY ALUMINUM IN

HYDROCHLORIC ACID. I - EFFECTS OF HEAT

TREATMENT, IRON CONTENT, AND

ACID COMPOSITION

By M. Metzger and J. Intrater

Columbia University

NACA

Washington

February 1955

NATIONAL ADVISORY COMMITTEE FOR AERONAUTIC

TECHNICAL NOTE 3281

INTERGRANULAR CORROSION OF HIGH-PURITY ALUMINUM IN

HYDROCHLORIC ACID.   I - EFFECTS OF HEAT

TREATMENT, IRON CONTENT, AND

ACID COMPOSITION

By M. Metzger and J. Intrater

SUMMARY

The intergranular corrosion of high-purity aluminum in hydrochloric acid was studied as a function of iron content, heat treatment, and acid composition under conditions where the rate of intergranular penetration was of the order of 1 millimeter per week. The behavior of specimens quenched to retain a single-phase structure indicated the rate of attack on the high-angle grain boundaries to be influenced by the segregation in these boundaries of iron and possibly other impurity atoms. Under the conditions studied, this segregation reduces the rate of attack; this led to the conclusion that the boundaries are inherently anodic. When the heat treatment was such that precipitation of a second phase could have occurred, the corrosion behavior could not be correlated with the small amount of second phase actually observed on microscopic examination, and it was postulated that pre-precipitation concentration gradients in the metal can have a strong influence on corrosion. Intergranular attack is rapid when there is a continual evolution of hydrogen gas from the intergranular crevice. Rapid attack can be obtained at low acid strengths by increasing the copper or iron content of the acid. This favors the strong attack on the low-angle grain and subgrain boundaries observed after certain heat treatments. Metallic impurities in the acid can also be responsible for preferential corrosion of the grain bodies observed in portions of some specimens with relatively inactive boundaries. When both the strength and the metallic-impurity content of the acid are low, a protective film forms over the surface and intergranular attack is very slow.

INTRODUCTION

The conditions of the metal structure responsible for susceptibility to intergranular corrosion which are best understood are those which occur in two-phase alloys when precipitation has occurred at the grain boundaries and has produced regions which have been proven to be anodic to the other

constituents of the structure by measurement of the solution potential of the isolated constituents (ref. 1). In some cases the anodic region is a zone adjacent to the boundary and lower in alloy content than the remainder of the grain and in others the precipitate itself is anodic. On the other hand, in a truly single-phase metal or alloy where intergranular corrosion is observed, other causes of susceptibility must be sought. It has been suggested that the grain boundary itself, that is, the narrow transition region between adjoining grains, is anodic as a characteristic inherent in its structure. This cannot be demonstrated except by eliminating the other possibilities. The other conceivable cause is that impurity or solute atoms in solid solution have a strong preference for sites at the grain boundary and their higher concentration at the boundary produces a significant alteration of its chemical activity. This segregation has been advanced as responsible for the action of boron in steel and bismuth in copper, among others; McLean (ref. 2) suggested that it occurs when there is an appreciable difference in size between solute and solvent atoms, and Cottrell (ref. 3) has given a detailed treatment for the analogous case of segregation at a dislocation. The evaluation of these possibilities in single-phase metals susceptible to intergranular corrosion is of fundamental interest.

One case in this category, the subject of the present report, is high-purity aluminum which suffers intergranular attack in hydrochloric acid under certain conditions; the rapid attack obtainable makes it experimentally convenient. Previous studies of this phenomenon have not led to a satisfactory understanding of the effect of the impurities on the susceptibility to intergranular corrosion. The structure of this material after heat treatment may be two phase, which is often difficult to detect because of the small amount of the second phase, and some of the previous work has probably been done in this condition. Clarification of this case was desired in addition to the investigation of the effect of impurities in the single-phase state. An additional feature of interest is the preferential attack of the grain bodies observed under some circumstances.

Knowledge of the factors influencing the chemical properties of the grain boundary would be of particular importance for single-phase copper alloys, many of which are susceptible to rapid intergranular failure by stress corrosion in ammoniacal atmospheres, although high-purity copper itself is immune. It has been shown by Thompson and Tracy (ref. 4) that those alloys which fail rapidly under stress are the ones for which intergranular attack occurs in the absence of stress, and thus one aspect of this problem is the reason why copper becomes susceptible to intergranular corrosion when certain solute elements are added. Many of these elements are effective in small amounts (e.g., phosphorus at less than 0.01 percent) at which the properties of the grain body cannot be substantially altered and which can be influential only if the atoms of the element have a strong tendency to segregate at the grain boundaries.

Previous Investigations

The first account of this phenomenon is that of Rohrman (ref. 5) who found that 99.95-percent aluminum quenched from 600° to 650° C disintegrated intergranularly in 10 and 20 percent hydrochloric acid while specimens furnace cooled from this temperature range did not.

Lacombe and Yannaquis (ref. 6) found no difference in the tendency to intergranular corrosion of aluminum of 99.99- and 99.9986-percent purity. The latter contained 0.0002 percent iron, 0.0009 percent silicon, and 0.0003 percent copper with a spectrographic trace of zinc and is the material of highest purity for which intergranular-corrosion studies have so far been reported. The samples were strained 2 percent, annealed at 600° C, and furnace cooled in 12 hours. These investigators showed the effects of increasing the acid strength and passing a current in reducing the time required for intergranular attack. They demonstrated the very low susceptibility to attack of a boundary between grains of very nearly the same orientation and also of a coherent twin boundary. These boundaries are the ones where the misfit of the adjoining lattices is small at the junction and the lattice in the transition region is relatively undistorted. At the boundary between grains of substantially different orientations there is considerable misfit, and Lacombe and Yannaquis postulated that the existence of "discontinuities" in such a boundary was responsible for its susceptibility.

Roald and Streicher (ref. 7) measured the rate of dissolution in 20 percent hydrochloric acid of five grades of aluminum from 99.2- to 99.998-percent purity after quenching or furnace cooling from 575° C. They found no difference in the type of attack for quenched from that for furnace-cooled specimens; however, for several compositions of lesser purity intergranular attack was not observed. They pointed out that the solubility of iron in aluminum is very low and that when the second phase is present it has a strong influence on corrosion by providing cathodes of relatively low hydrogen overvoltage.

Mears, Brown, and Dix (ref. 8) described measurements on 99.986 percent aluminum in $22\frac{1}{2}$ percent hydrochloric acid where the direction of current flow was determined with the grain boundaries masked out on one specimen and the grain bodies on a companion specimen. After quenching from 620° C the boundaries were anodic while after slowly cooling from this temperature the grain bodies were anodic. In the latter case, preferential corrosion of the grain body occurred (in 10 to 20 percent acid) and the boundaries were left in relief (ref. 1). This type of attack has also been noted by Chaudron, Lacombe, and Yannaquis (ref. 9) under unspecified experimental conditions.

From the results of these investigations it may be noted that (1) the fact that, in some cases, intergranular corrosion has been observed in furnace-cooled specimens indicates that internal stresses, as might be produced by quenching, are not essential, and (2) impurities must have a strong influence under certain conditions because quenched and slowly cooled specimens may behave differently and, stresses being excluded, these can differ only in the form and distribution of impurities.

When the work of the authors of the present report was almost completed, it was learned that Dr. E. C. W. Perryman had been making a somewhat similar investigation. He studied the effect of an iron content from 0.001 to 0.055 percent on the intergranular corrosion in 10 percent hydrochloric acid after heating at 640° C and quenching or cooling slowly. Quenched samples of higher iron content showed higher rates of intergranular attack. Perryman concluded that segregation of iron atoms at the grain boundaries was involved and discussed the mechanism of corrosion from the viewpoint of cathodic boundaries. His rates of intergranular penetration were several microns per month, much lower than in the present work where the rates were of the order of 1 millimeter per week.

Possible Effects of Impurities

There are several ways in which impurities can conceivably influence intergranular corrosion. (1) There may be associated with the boundaries either a second phase or concentration gradients in the solid solution (because of pre-precipitation phenomena or failure to achieve homogenization of the matrix following precipitation) resulting in solution potential differences; if either of these conditions is responsible for susceptibility, a homogeneous single-phase structure would not be susceptible. (2) In a single-phase structure, the boundaries may be susceptible in the absence of impurities. If impurity atoms in solid solution tend to segregate in the boundaries and if the chemical activity of the boundaries is thereby altered, this may produce susceptibility or merely enhance or diminish it.

In the present investigation, an attempt is made to evaluate these possibilities by observing intergranular corrosion after various heat treatments designed to alter the distribution of impurities. All specimens are initially annealed at an elevated temperature to produce a large grain size for convenience of observation. Now the quantities of impurity elements in high-purity aluminum are, for the elements commonly reported, well within the solid-solubility limit at sufficiently elevated temperatures. A properly quenched specimen is therefore assumed to be single phase. It is only for iron that comparatively high temperatures are required (400° to 500° C for iron in the range 0.001 to 0.006 percent), and an aluminum-iron phase (perhaps involving silicon and manganese) would be the major second constituent in specimens which are not rapidly

quenched or which are reheated at lower temperatures after quenching. However, since the quantity of the second constituent in material of relatively high purity will be very small, it cannot be assumed that a reliable determination of its presence or distribution will always be made metallographically. Further, it must be assumed that precipitation and homogenization will not generally be complete and there will be concentration gradients within the solid solution in all specimens which are not rapidly quenched. The precise distribution of these gradients will not be known, and it may be anticipated that the relation of susceptibility to intergranular corrosion to structural conditions in the metal will be difficult to determine in this case.

In the study of single-phase structures, evidence for the segregation of impurity atoms in the grain boundaries will not be obtainable microscopically but certain inferences concerning the distribution of impurity atoms can be drawn from statistical mechanical considerations of a general nature. Under equilibrium conditions in the solid-solution region, the only possible structural variation is in the fraction of atomic sites in the grain-boundary region which is occupied by impurity atoms. If the interaction energy associated with the segregation of an impurity atom varies only slowly with temperature, as is expected when the most important factor is relative atomic size, then the fraction of boundary sites occupied by impurity atoms will be lower the higher the temperature. The influence of the segregation phenomenon on intergranular corrosion can then be studied in samples rapidly quenched to preserve the grain-boundary compositions characteristic of different temperatures in the solid-solution range.

The presence of trace impurities in the aluminum not included in the analysis report would effectively invalidate the assumption that the structure is single phase above the solution temperature for iron only when the amount of impurity present and its solubility happen to be related in a special manner; any impurity which is essentially insoluble at all temperatures cannot be responsible for changes in susceptibility to intergranular corrosion with heat treatment.

Solid Solubility of Iron

The solid solubility of iron in aluminum (i.e., of the aluminum-iron phase, approximately Al_3Fe) was determined down to 500° C by Edgar on quenched samples using the electrical-resistance method (ref. 10). For an estimate of the solubility limit at lower temperatures, his data have been extended by plotting the logarithm of the solubility versus the reciprocal of the absolute temperature and extrapolating the straight line obtained. The values are given in table I.

Summary of Experimental Work

The experimental work comprises three parts: (1) A broad survey of
the effect of heat treatment on intergranular corrosion in a single com-
position of high-purity aluminum leading to preliminary inferences on the
relation between structure and susceptibility following the reasoning
outlined above, (2) a close study of the effect of segregation of impurity
atoms at the grain boundaries in three compositions of differing iron
content together with a few tests following up some phenomena observed
in part (1), and (3) a study of the effect of the composition of the test
acid and observations relating to the mechanism of corrosion.

This investigation was conducted at Columbia University under the
sponsorship and with the financial assistance of the National Advisory
Committee for Aeronautics. The authors wish to express their apprecia-
tion to Professor T. A. Read for valuable discussions and suggestions,
to Professor M. Gensamer for his interest and encouragement, and to
Mr. E. H. Dix, Jr., Mr. R. H. Brown, and Dr. R. D. Williams of the
Aluminum Company of America for helpful discussions and for kindly pre-
paring the specimen material. Thanks are also due Messrs. A. Gross
and E. W. Jensen for assistance with the experimental work.

EXPERIMENTAL PROCEDURE

The analyses of the material used in this work are given in table II.
The material was in the form of hard-rolled (-H18) sheet supplied by the
Aluminum Company of America. Specimens in the form of $\frac{1}{4}$- by $1\frac{1}{2}$-inch strips
were sheared or cut from the stock and the edges were finished by filing.
Heat treatment was carried out in air in Alundum combustion boats or
(during the preliminary work) with the samples sealed in Pyrex tubes under
a vacuum of better than 0.1 micron. The sample was in contact with the
glass at only a few points at which it was protected by an oxide film,
and it is not thought that this procedure resulted in an appreciable
pickup of silicon.

For the corrosion test, the specimen was completely immersed in
300 milliliters of hydrochloric acid in a 600-milliliter beaker covered
with a watch glass. It rested on the long edge, held upright by a small
U-shaped piece of Pyrex cane. To provide an initial surface favorable
for corrosion, it was found convenient to etch the specimens, rinse
several times with acid of the same composition as the test acid, and
insert in the test solution. Etching was continued to just beyond the
time required for hydrogen to be evolved over the specimen surface. The
etchants used acted partly to dissolve the film and partly to undermine
it by dissolution of the underlying metal. In many cases, film removal
was not complete and some small oxide flakes were observed after a few

hours in the test beaker, but this was not found to have a significant effect on the form or rate of corrosion.

The time required for one or a few grain boundaries to be corroded through the thickness of the sheet, as determined by holding the sample up to a light, was designated the "failure time" and served as a measure of the intergranular corrosion rate. In later tests, the sensitivity was improved by using a strong parallel beam of light in a darkened room. A forceps with long Teflon tips was used to hold the specimens for examination; they were removed from the test solution for less than 30 seconds and remained wet. No indication was found that this procedure influenced the subsequent progress of intergranular corrosion.

The acid content of the test solution was chosen to yield relatively rapid intergranular corrosion (failure times of the order of a week) with little attendant general corrosion. In the preliminary work, this was obtained with 7 percent hydrochloric acid (7 grams HCl per 100 grams solution). Subsequently, a different source of distilled water was used to make up the test acid and the corrosion rate in 7 percent acid was then found to be extremely slow. Analyses of the two waters and of one lot of the concentrated acid reagent (believed to be representative of the several lots used), given in table III, together with checks of the effect of copper and iron additions to the water indicated that the agent accelerating corrosion in the M water was copper. With H water, the acid strength was increased to 20 percent to obtain the required rate of intergranular attack.

PRELIMINARY SURVEY OF EFFECT OF HEAT TREATMENT

In this portion of the work, a survey was made of the influence of a wide range of heat treatments. Material C containing 0.006 percent iron (minimum solid-solution temperature, 500° C) and a test solution of 7 percent hydrochloric acid made up with M water (thus containing about 0.8 parts per million of copper) were employed. The standard annealing treatment was 600° C for 18 hours. This is within the solid-solution region and produced a convenient grain size of several millimeters. Often, preferred orientation was noted. No special attempt was made to take into account this and other factors, such as the fluctuations in room temperature from test to test, which contributed to variations in the rate of corrosion. The form of corrosion was always reproduced, and the failure times were sufficiently reproducible for the purpose of the survey.

As a check of the possible influence of exposure to nitrogen during heat treatment, early samples were heat treated after sealing under vacuum in Pyrex tubes. Although this procedure did not suppress susceptibility to intergranular corrosion, the practice of heat-treating sealed samples

was continued. For a reasonably efficient quench the tube must crack on
immersion in the cold water, and the sample was discarded when the tube
failed to crack.

Effect of Method of Surface Preparation

When an etchant is used to remove the surface oxide film prior to
immersion in the test solution, the corrosion test can be influenced if
there is cementation on the aluminum surface of relatively noble metallic
impurities in the etching solution or, in the case when two phases are
present, if there is preferential attack on the matrix and enrichment of
the surface in the cathodic second phase. It was thought that these
effects might be minimized by the use of an oxidizing acid mixture; the
following etchant A has been used as standard: 10 milliliters of sul-
furic acid, 2 milliliters of nitric acid, 2 milliliters of hydrochloric
acid and 50 milliliters of water at 70° C for 3 minutes. Intergranular-
corrosion tests on specimens water quenched from 600° C showed similar
types and rates of corrosion after etching either with etchant A, with
a modified Tucker's reagent (hydrochloric, nitric, and hydrofluoric acids
in water) at room temperature, with 37 percent hydrochloric acid at room
temperature, or with hot 10 percent sodium hydroxide or after filing
lightly instead of etching. Further checks throughout this investigation
have not indicated any effect of the method of surface preparation on the
form of corrosion; an effect on the rate of corrosion was observed only
in a few instances. One such case was noted in specimens reheated to
400° C after quenching; for these, sodium hydroxide gave a failure time
of 6 days as compared with 16 days for etchant A. This difference does
not appear to be attributable to enrichment of the specimen surface in
the second phase when etched with sodium hydroxide since the amount of
second phase identifiable in the microstructure is very small. It may
be noted, however, that sodium hydroxide is less desirable as an etchant
because the iron and heavy-metal contents of the reagent are substantially
higher than those of the acid reagents available.

An additional instance of an effect due to the surface preparation
was noted in several samples etched in sodium hydroxide and rinsed in
distilled water before immersion in the test solution when they remained
almost a week in the test solution without noticeable progress of inter-
granular attack, presumably because of a uniform protective film. After
re-etching and rinsing as usual only with the stock test acid, inter-
granular attack proceeded at the normal rate. Evidence for the formation
of a protective film under other conditions will be described later.

Effect of Reheating Quenched Specimens

As the first part of the survey of heat treatments, the effects of reheating specimens previously water quenched from 600° C at temperatures from 100° to 400° C were investigated. The appearance of a quenched specimen is shown in figure 1(a). Boundaries between grains of substantial orientation difference are strongly attacked, but the attack of subgrain and low-angle grain boundaries is weak and only superficial even after prolonged exposure to the test acid. This is similar to the behavior reported by Lacombe and Yannaquis. The shallow uniform etching of the surface of a quenched specimen is taken as a reference condition of negligible general corrosion.

For a reheating period of 4 hours, a temperature of 200° to 250° C produced slight general corrosion (surface roughening), while at 300° and 400° C there was a little general corrosion accompanied by a strong attack of the low-angle grain and subgrain boundaries as well as of the high-angle grain boundaries. The last is shown in figure 1(b). The rate of cooling from the reheating temperature had no noticeable effect. Corrosion of subgrain boundaries had been noted by Lacombe and Yannaquis (in furnace-cooled specimens) after prolonged anodic treatment in hydrochloric acid.

Microscopic examination shows that the change in behavior at 200° C and above is accompanied by structural changes, indicated by substantial changes in the response to various etching solutions; a second phase was identified at 300° C, but the scattered fine particles observed cannot account for the uniform strong subgrain-boundary attack.

As a brief check of stress relaxation, specimens were reheated 1 hour at 200° C or 74 hours at 150° C since the data of Kê indicate that the shear stress across the grain boundaries of high-purity aluminum relaxes to 70 percent of its initial value after these treatments (ref. 11); no significant decrease in susceptibility to intergranular corrosion was found. It would not be suspected that stresses play a large part in intergranular corrosion of aluminum since there is no anisotropy of thermal expansion and the only stresses introduced are those due to temperature gradients within the specimen during the quench. These are not likely to be large because of the small section and high thermal conductivity.

Effect of Rate of Cooling

Data showing the effect of the rate of cooling from the annealing temperature are given in table IV in order of estimated cooling rate.

With an air blast or liquid-nitrogen quench, the subgrain boundaries
and low-angle grain boundaries are attacked rapidly and only slightly
slower than the high-angle grain boundaries. A number of subgrains have
fallen out by the time the high-angle boundaries and some subgrain bounda-
ries have corroded through the thickness of the specimen. The subgrain
boundaries were less rapidly attacked after oil quenching. With air-
blast, liquid-nitrogen, or oil quenching, the strong relative orientation
dependence of the susceptibility of a boundary to corrosion noted by
Lacombe and Yannaquis does not apply.

The similarity between the effect of an inefficient quench and the
effect of reheating to 300° and 400° C after a rapid quench suggests that
the redistribution of impurity atoms during the inefficient quench
favoring corrosion of low-angle grain and subgrain boundaries occurs
during cooling through the 300°-to-400° C range. From the fact that this
effect is observed at cooling rates which are still rapid, it may be
inferred that this redistribution cannot involve the movement of the
impurity atoms over large distances and that actual precipitation of a
second phase does not occur. Also, the strong effects on the corrosion
of low-angle grain and subgrain boundaries suggest that a redistribution
of impurity atoms strongly associated with these boundaries must occur.
Lacombe and Berghezan (ref. 12) have ascribed the susceptibility to
etching of subgrain boundaries in an aluminum-zinc alloy to concentration
of zinc atoms along these boundaries.

The specimens slow cooled in 8 or 24 hours showed a number of char-
acteristic features, sometimes in different proportions in duplicate
samples. There is always thinning of the specimen to two-thirds or one-
half its initial thickness, in some grains more than others, by the time
the first boundaries have corroded through. Some subgrain boundaries
are attacked. Only a fraction of the grain boundaries is strongly
attacked; at some of the others there is a slightly elevated ridge appar-
ently similar to the inverted intergranular corrosion described by Brown
and Mears and by Chaudron, Lacombe, and Yannaquis. In a number of cases,
the boundary is corroded normally for part of its length and shows the
relief effect in the adjacent part or on the opposite face of the speci-
men. Subsequent observations indicate that this mixture of several types
of corrosion is associated with the high copper content of the test acid
and does not necessarily reflect variations in the structural conditions
along a grain boundary.

Effect of Heat-Treating Temperature

Samples in the as-received condition were heated for 18 hours at
temperatures from 250° to 645° C and water quenched. Below 450° C general
corrosion predominated; it was almost absent above 500° C. Strong inter-
granular attack is noted at 450° C but is somewhat broad at 450°
and 500° C. Quenching from 550° C and above yielded sharp intergranular
attack. The solution temperature of the aluminum-iron second phase is

500° C for this material. Thus, it is in the single-phase region that
selective intergranular attack was observed, although some intergranular
attack also occurs in the two-phase region where it is partially or com-
pletely obscured by concurrent general corrosion.

Because the grain size begins to coarsen at 500° C and because there
were some variations in the degree of preferred orientation, a proper
comparison of the failure times for various temperatures of treatment was
not possible. However, there was some indication that intergranular cor-
rosion was faster after quenching from the higher temperatures in the
solid-solution range, and this suggested that the segregation of dissolved
atoms in the grain boundaries influenced the rate of corrosion. This
point was marked for closer study.

Tests were also made on specimens furnace cooled at about 75° C per
hour after heating for 18 hours at 550°, 600°, 625°, and 645° C. In
general these showed, in varying proportions, the features observed in
samples slow cooled from 600° C and described above. In every case, the
rate of intergranular attack was lower than the rate for a specimen
quenched from the same temperature, but no trend as a function of
annealing temperature was apparent in form or rate.

As previously noted in reheated samples, the occasional particles
of the second phase identified on microscopic examination of slow-cooled
specimens do not themselves account for any feature of the corrosion
behavior of these specimens. In any event, knowledge of the distribu-
tion of the second phase is not necessarily sufficient for understanding
the relation between the corrosion behavior and the structure of the
metal since it has been concluded from the results obtained with inef-
ficient quenches that a redistribution of impurity atoms not involving
actual precipitation can have a substantial influence. It will be diffi-
cult to infer the distribution of dissolved impurities after slow cooling,
even when information concerning the tendency for segregation of impurity
atoms in the boundaries is available, so that further intensive study of
the slow-cooled case seems unprofitable. On the other hand, the study
of the segregation phenomenon involves specimens rapidly quenched from
temperatures within the single-phase region, and inferences concerning
the distribution of impurity atoms in these specimens will not be sub-
ject to the many uncertainties which attach to the slow-cooled case, as
indicated in the Introduction.

FURTHER STUDY OF HEAT TREATMENT AND COMPOSITION

For a close study of the effects on the rate of intergranular cor-
rosion of segregation of impurity atoms in the grain boundaries, some
experimental procedures were refined and three compositions of high-purity

aluminum differing only in iron content were obtained through the cour-
tesy of the Aluminum Company of America. These ranged from about the
lowest available (I, 0.0004 percent iron, minimum solid-solution tempera-
ture, 375° C) through an intermediate value (II, 0.004 percent iron,
solution temperature, 480° C) to a relatively high value (III, 0.023 per-
cent iron, solution temperature, 590° C). Iron was chosen as one element
likely to segregate in the boundaries since its atomic diameter is more
than 10 percent smaller than that of aluminum.

It was considered desirable that the minimum annealing temperatures
be substantially above the minimum solid-solution temperatures, and the
temperature ranges used were 500° to 647° C for I, 550° to 647° C for II,
and 647° C only for III. There was no evidence of melting at the grain
boundaries in any composition at 647° C. The annealing periods followed
the schedule of Edgar, 24 hours being used at 647° C with an additional
24 hours for each 50° C decrease in temperature. While this procedure
does not provide an equivalent degree of approach to equilibrium at dif-
ferent temperatures when this depends on diffusion, the annealing times
are believed sufficient to avoid any considerable departure from equi-
librium conditions. Extending the annealing period at 647° C to 96 hours
had no effect for quenched samples of any composition.

The subgrain size of the new material after heat treatment was too
small for convenient observation of the susceptibility of the subgrain
boundaries to corrosion.

Since, in order to insure a rapid quench, the specimens were now
annealed in air, removal of the surface oxide was more difficult and the
temperature of etchant A was increased to 90° C. The heating of the
specimen during the etching operation had no noticeable effect, quenched
specimens which were etched with the modified Tucker etch at room temper-
ature or which were exposed unetched showing the same rate of intergranu-
lar corrosion in 20 percent acid as those etched with etchant A.

The temperature during the corrosion test was maintained in the
range of 22° to 26° C.

Effects of Temperature and Iron Content in

Single-Phase Condition

In order to compare the segregation of impurity atoms at the grain
boundaries in materials of differing iron content, the general argument
from statistical mechanics is applied. This indicates that at equilib-
rium at a given temperature there is a certain ratio of the concentration
of iron atoms in the boundary region to the over-all concentration. Thus
the boundary concentration will be higher the higher the iron content of

the material, and so far as the boundaries are concerned the effect of lowering the annealing temperature is the same as the effect of increasing the iron content. In specimens rapidly quenched to preserve the boundary concentration characteristic of the final annealing temperature, these effects should be the same on the intergranular corrosion rate so long as this rate is not found to be more strongly influenced by the over-all than by the boundary iron concentration.

Specimens were treated at the several test temperatures in three ways: (1) direct treatment in the as-received condition, (2) reheating after a previous quench from 647° C, and (3) heating to 647° C followed by furnace cooling to the test temperature and holding, in each case followed by a rapid quench. The rates of intergranular corrosion in 20 percent hydrochloric acid, as measured by the failure times (days for at least one boundary to be corroded through the thickness of the specimen), are given in table V, no allowance having been made for variations in grain size which may have slightly influenced the failure times. These data show that the rate of intergranular corrosion is greater the higher the final annealing temperature and the smaller the iron content. Although the differences between materials of different purity may conceivably be influenced by several factors, the changes produced by treatments (2) and (3) of a single composition at different temperatures well within the single-phase region can be interpreted only as due to the segregation of impurity atoms in the grain boundary. The rate of intergranular attack is found to be lower the greater the concentration of iron and other impurity atoms in the grain-boundary region. This leads to the conclusion that impurities in aluminum are not required for intergranular corrosion in this acid to occur.

The basic features of corrosion were similar in all cases. All boundaries except those where there is a small orientation difference between adjacent grains ultimately corrode through. At the low-angle boundaries, the attack is superficial and scarcely progresses faster than general corrosion. General corrosion appears in I and II as a slow superficial etching (fig. 2(a)) and in III as a gradual thinning of the specimen accompanied by attack at the edges (fig. 2(b)). The relatively severe general corrosion in III is believed due in large part to residual composition gradients in the solid solution; observations to be described later suggest that it can be regarded as a superimposed phenomenon separate from the intergranular corrosion which is not observably different except in rate from that in I and II.

The measurements of the relative intergranular corrosion rates were subsequently refined and the data analyzed to estimate the interaction energy for the segregation of iron atoms in the grain boundaries. This work is described in a separate publication. It may be noted here that the intergranular-corrosion data could not be accounted for by the segregation of iron alone, and it was concluded that at least one other

strongly segregating impurity element was also involved. Consideration of the quantities of other impurities present and estimation of their relative tendencies to segregate by comparison of the atomic diameters with that of aluminum suggested that the other impurity involved was copper.

It was of interest to see whether the effects of the segregation of impurity atoms at the grain boundaries observed in 20 percent acid would be the same under other conditions of corrosion. This was checked briefly using as the test medium 7 percent hydrochloric acid made up with H water to which had been added 1 part per million of copper. This approximated the test conditions used in preliminary studies; since some general corrosion was now noted, the copper content of the test solution was probably a trifle higher than before. The specimens were quenched from 647° C or furnace cooled from this temperature to 605° C, held, and quenched. Failure times are given in table VI. These values show the same trend with temperature and purity as was indicated in 20 percent acid. The failure time of III at 647° C was not determined since the general corrosion in one part of the sample outraced intergranular corrosion, but it was evident that intergranular attack was considerably slower than in I and II. This sample showed an area of pronounced inverted intergranular corrosion not observed in 20 percent acid, with thin strips of metal at the grain boundaries standing strongly in relief (fig. 3). At the same boundaries on the opposite side of the specimen, normal intergranular corrosion had begun. In a quenched sample this mixture of inverse forms of corrosion along the length of a single boundary cannot be due to a mixture of structural conditions at this boundary; it is attributed to the action of the copper in the test acid. This action is discussed below.

Effects of Cooling Rate and Iron Content

To determine the effect of iron content in slowly cooled samples, specimens of the new material were tested in 20 percent acid after heating at 647° C and cooling at rates down to 4.5° C per hour. The failure times, given in table VII, show that at slow cooling rates the rate of intergranular attack is decreased for I and II but increased for III. In contrast to the preliminary studies, where the appearance of the corroded specimen varied greatly with cooling rate, the slow-cooled specimens in 20 percent acid were usually similar in appearance (fig. 4) to quenched specimens but were distinguishable by a greater rate of general corrosion and by a tendency toward pitting, usually at grain boundaries. In addition, a weak inverted intergranular corrosion effect was noted on a very few boundaries in the sample of II cooled at 75° C per hour after prolonged immersion (18 days). That the effect of slow cooling as compared with that of quenching is strongly dependent on composition can account for some of the varying results of different investigators on this point.

As in the preliminary work, microscopic examination revealed a few scattered particles of the aluminum-iron phase adjacent to grain boundaries (in II and III cooled at 4.5° C per hour and in III cooled at 75° C per hour), but the structures observed do not account for the difference between the slow-cooled samples and the quenched samples. In particular, in III the particles of second phase observed optically are much too widely spaced to account for the rapid intergranular attack as being due to the integrated effect of concentrations of corrosion in the vicinity of each particle acting as a strong cathode and careful examination of oxide replicas in the electron microscope revealed no closely spaced necklace of fine particles. However, the presence of the second phase does contribute to the pitting observed in these samples.

In view of these observations, the effect of slow cooling on the intergranular corrosion rate in these specimens is to be ascribed primarily to redistribution of the impurity atoms without actual precipitation. If the cooling rate were sufficiently slow to maintain equilibrium the distribution of impurities could be estimated by the following argument. The concentration in the boundaries of some of the impurity atoms increases as the temperature decreases except for iron where this trend is reversed on passing below its solid-solution temperature since then the equilibrium boundary concentration of iron is a function of its rapidly decreasing solid solubility in the grain body and not of the total iron content. Most of the other impurities present are much more soluble and their segregation is not limited in this fashion. Since I, II, and III differ only in iron content, at equilibrium at room temperature they differ only in the amount of the aluminum-iron phase. If this phase is not directly related to intergranular corrosion, all three should corrode at the same rate. That this is not the case is to be expected since, at any practical cooling rate, equilibrium is not maintained at the lower temperatures because of the rapid drop in the diffusion rates of the impurity elements. It may also be noted that the principal impurity atoms in the boundaries at low temperatures would not be primarily iron (as was the case in the rapidly quenched specimens studied previously) and the effect on the intergranular corrosion rate of boundary segregations of other impurity atoms may not be the same as the effect of segregations of iron atoms. It is thus very difficult to interpret the intergranular corrosion behavior of slowly cooled specimens. Perhaps the very rapid failure of specimens of III (as compared with I and II) after slow cooling can be attributed to iron-concentration gradients in the solid solution associated with the boundaries; these gradients would be greatest in III where the iron content is greatest.

Additional instances in which concentration gradients are believed to have strong influence were noted in water-quenched specimens of II tested in 20 percent acid. Specimens annealed directly at 550° C suffered rapid uniform general corrosion while specimens initially annealed at 647° C and cooled to 550° C before quenching showed very little general

corrosion. Somewhat similar behavior is shown in C. Although 550° C
is within the solid-solution region for both II and C, it is believed
that this temperature was not sufficient to homogenize the matrix with
respect to the dissolved iron and concentration gradients remained.

Susceptibility of Low-Angle Grain Boundaries

In following up the result of preliminary work where strongly
enhanced attack of the low-angle boundaries was observed in material C
after quenching in liquid nitrogen from 600° C or reheating after water
quenching, all attempts to produce this effect in samples of I, II,
or III tested in 20 percent acid were unsuccessful. It was found that
even with the original material C samples quenched in liquid nitrogen
behaved like those quenched in water when tested in 20 percent acid, but
the difference was again observed when the acid composition used in the
preliminary work was duplicated by making up 7 percent acid with 0.8 part
per million of copper. In general, different structural conditions in
the sample produced a greater range of corrosion behavior in the latter
acid.

COMPOSITION OF TEST ACID AND MECHANISM OF CORROSION

Composition of Test Acid

In table VIII are summarized the results of various tests made to
determine the effects of the strength and metallic impurity content of
the test acid on the rate of intergranular corrosion in quenched samples.
The first parts of parts (a) and (b) show the influence of copper-ion
concentration in 7 percent acid, starting from very slow attack at the
minimum level of 0.1 part per million (already present in the H water
and possibly in the acid reagent) through strong intergranular with
relatively little general attack at 0.8 part per million to rapid uniform
general corrosion at 8 parts per million. At a copper concentration of
0.1 part per million the behavior follows a similar sequence when the
acid strength is increased as shown in the second part of table VIII (a).
These data parallel those of Lacombe and Yannaquis on the effect of
hydrochloric-acid concentration. It is perhaps noteworthy that this
range of acid strengths represents a wider range of hydrogen-ion activi-
ties since the activity coefficient increases with increasing concentra-
tion in this range (ref. 13). The second part of table VIII (a) illus-
trates the reason for the choice of 20 percent acid (in the later portion
of this work) since it produces the most rapid rate of intergranular cor-
rosion not accompanied by strong general corrosion. For higher acid con-
centrations general corrosion becomes relatively more prominent and much
above 25 percent the specimen thins uniformly except for shallow grooves
at the grain boundaries.

The data also indicate that iron in the acid is much less effective than equal amounts of copper in accelerating both intergranular and general corrosion. Even with 10 parts per million of iron in 20 percent acid, up to the time the first few boundaries had corroded through there was hardly more general attack than had been observed for the same period of exposure when no iron was added.

In extension of the data in the last part of table VIII (b), some tests have been made with 20 percent acid prepared by distillation using a fused silica condenser and polyethylene containers. This procedure was presumed to have reduced the metallic impurity content significantly below the amount present in the acid reagent and the H water. The rate of intergranular corrosion tended to be slower and, in contrast with tests made with the original acid (i.e., that containing 0.1 part per million of copper), was highly sensitive to surface preparation; also the attack was not so sharp. These are then further indications of the strong influence of the metallic impurities in the acid.

Hydrogen Evolution

Following the observation of a few streams of fine bubbles rising from several samples immersed in the test acid, it was found that by using lateral illumination in a dark room many more streams could be seen. Close attention was then paid to the hydrogen evolution for all subsequent samples.

For the samples in 20 percent acid or 7 percent acid with 0.8 part per million of copper, it was noted that specimens showing substantial rates of intergranular attack always exhibited streams of bubbles from some of the corroding grain-boundary crevices with perhaps an occasional bubble or stream from some point in the grain interior. The size of the bubbles ranged up to several tenths of a millimeter; they were finer and more numerous in the 7 percent acid with 0.8 part per million of copper than in 20 percent acid for the same rate of intergranular corrosion. The bubble streams are observed only at discrete sites on a corroding boundary, but since the boundary corrodes uniformly it would appear that the observed site of bubble evolution does not indicate a localized corrosion process but represents the point of collection and emission from the crevice of the hydrogen formed in a region in the unobserved part of the crevice. The bubble size usually increases somewhat during the course of the test, suggesting that the size observed is determined by the width of the mouth of the corroded crevice which increases slowly due to general corrosion.

The rate of corrosion is closely related to the rate of hydrogen evolution. At one extreme, samples in 7 percent acid containing only 0.1 part per million of copper, where the rate of intergranular corrosion

was very slow, showed no more than one or two bubbles from the whole
specimen in several minutes. At the other extreme, when intergranular
attack is accompanied by considerable general attack there is rapid bub-
ble evolution from many points in the grain interior as well as streams
from the corroding boundaries. Further, samples with substantially dif-
ferent rates of intergranular attack showed substantially different rates
of bubble evolution from the intergranular crevices. The close relation
between the rate of hydrogen evolution and the rate of intergranular or
general corrosion strongly suggests that the production of hydrogen gas
is the principal cathodic reaction in all of those tests where corrosion
progressed at a substantial rate. For one sample, the total volume of
hydrogen evolved from the intergranular crevices was estimated and found
to be sufficient in magnitude to account for the volume of aluminum esti-
mated to have been dissolved near the grain boundaries.

Mechanism of Corrosion

The case considered is that of rapid intergranular corrosion in
single-phase specimens, where the only structural heterogeneities are
the grain boundaries. It is assumed that the evolution of hydrogen gas
observed at the corroding boundaries is the cathodic reaction as suggested
above. Thus, both the anode (area where metal is being dissolved) and the
cathode (area where hydrogen gas is discharged) are within the crevice at
the corroding grain boundary. These considerations do not indicate whether
the grain boundary itself is the anode or the cathode. Now the most rapid
intergranular attack was found in the material of highest purity quenched
from the highest temperature, that is, where the impurity atom concentra-
tion in the boundaries was least and thus for the condition closest to a
"pure" boundary. From consideration of the structure and energy of such
a boundary, it is not reasonable that it would be cathodic to the remain-
der of the grain and therefore the boundary is concluded to be anodic.

Certain considerations on the mechanism of corrosion are suggested
by the observations made in the course of this work. One factor involved
is the tendency for formation of a protective film; the formation by pre-
cipitation of an aluminum hydroxide surface film is presumed possible
when anode and cathode areas are adjacent since then the concentrations
of aluminum ions near the anode adjoin the area near the cathode where
the hydrogen-ion concentration has been reduced. Now if the evolution
of hydrogen bubbles at the local cathode is sufficiently rapid, the
resulting stirring action can disperse the products of the local cell
reaction and prevent the stifling of corrosion by film formation. The
effect of increasing acid strength, which facilitates hydrogen evolution
and also makes film formation more difficult, is postulated to make the
continual evolution of hydrogen possible at the cathodes adjacent to
weaker anodes, that is, at weaker local cells. Thus, in reference to
the second part of table VIII (a), in 7 percent acid the hydrogen-ion

concentration is insufficient to result in continual evolution of hydro-
gen adjacent to even the strong anodes (i.e., the grain boundaries) and
intergranular as well as general attack is very slow. In 20 percent
acid, there can be continual hydrogen evolution adjacent to the grain
boundaries but not adjacent to the weak anodes distributed throughout
the grain bodies so that a partly protective film is maintained over the
grain surfaces and general corrosion is not severe even though inter-
granular attack is rapid. In 25-percent acid, the hydrogen-ion concen-
tration is high enough to permit continual hydrogen evolution even in
the weak local cells distributed over the grain surfaces and severe gen-
eral corrosion results in addition to intergranular attack.

Metallic impurities in the acid which cement out on the specimen
surface and reduce the hydrogen overvoltage are considered to have an
effect analogous to that of increasing the strength of the acid. That
actual cementation occurs in the case of iron has not been verified.

The view that evolution of hydrogen gas prevents stifling of cor-
rosion because of the stirring action is consistent with the observation
that agitation (rotation) of the specimen in 20 percent acid greatly
increased the rate of general corrosion. It also increased the inter-
granular corrosion rate.

The factors of film formation and hydrogen evolution are also
involved in the pitting corrosion of aluminum in neutral chloride solu-
tions studied by Edeleanu and Evans (ref. 14) but appear to operate in
a different manner. In these solutions, initial attack at any area
results in conditions favorable to continuation of the corrosion in that
area and pitting can be induced by scratches. A number of attempts were
made to induce corrosion on the grain surfaces of specimens of high-
purity aluminum in hydrochloric acid of various compositions, but in no
case did corrosion progress preferentially at the scratches.

It may be noted that for rapid intergranular corrosion involving
the evolution of hydrogen from the intergranular crevice the principal
cathode is within this crevice and a corrosion current flowing between
the crevice and the remainder of the grain body is not required. The
extent of attack on the grain surfaces can be altered without affecting
the local action at the boundary. This was noted with specimens of I
and III after quenching from 647° C; when coupled in 20 percent acid, the
rate of intergranular attack or of bubble evolution from the corroding
crevices of either specimen was not substantially altered, but the
relative amounts of general corrosion of uncoupled specimens were reversed;
that is, coupling resulted in a moderate attack of the grain surfaces of
I while the surface of III remained almost completely unattacked. III
was $1\frac{1}{4}$- millivolt cathodic on open circuit.

Metallic Impurities in Acid

In addition to functioning in a manner analogous to increasing the acid strength as discussed previously, substantial copper in the acid favors two particular phenomena. One of these is rapid subgrain boundary attack; this has not been studied in detail. The other is the preferential attack of grain bodies observed on portions of certain specimens with relatively inactive grain boundaries when tested in 7 percent acid containing 0.8 part per million of copper. The effect appears in C and II (not in I or III) after slow cooling at 75° C per hour but was most prominent in III after quenching from 647° C. In addition to inversion of the corrosion at some grain boundaries, the slow-cooled samples show in relief small areas of irregular contour the upper surfaces of which are often bright, having remained almost completely unattacked. In some cases, these areas cross grain boundaries and are evidently not connected directly with the structure of the metal. These areas are thought to be determined at the start of corrosion by preferential cementation of copper, possibly because of the nonuniform oxide film remaining after etching, since any area sufficiently covered with copper will continue to function as a cathode and remain unattacked until it is undermined by dissolution of the underlying metal. If the same process is to lead to preferential attack of some grain bodies, then some grain boundaries must be smothered by copper, which is perhaps possible when these boundaries are only weak anodes and are cathodic to other boundaries; the selective cementation of the copper in this case might be related to a more rapid removal of the residual film at the boundaries. The importance of the initial surface condition is indicated by the observation that there were no grain boundaries but only irregular areas in relief in a duplicate sample of III quenched from 647° C which, contrary to the usual procedure, was not etched before immersion. It is significant that these phenomena did not occur in samples where the grain boundaries were rapidly attacked. The presence of active boundaries apparently results in cementation of copper which is substantially uniform over the grain surface.

An additional point of interest is the reason for the tremendous change in the influence of copper between concentrations of 0.2 and 0.8 part per million in 7 percent acid. At 0.8 part per million a change in surface color (initial cementation) could occasionally be observed some hours after immersion; after a day the surface has been roughened and at least some of the copper appears as small black specks clinging loosely to the specimen. There was no evidence of slackening of the corrosion rate in the latter stage, and there is no reason to suppose that the copper ceases to be effective then since it can be oxidized and redissolved. If it were to be assumed that substantially all the copper has cemented out in a uniform layer (except for the corroding boundaries) and the surface-roughness factor is of order 100, then for 0.8 part per million there would be a layer 5 A thick, and for

0.2 part per million the layer would be incomplete. However, the remarkable increase of the intergranular corrosion rate from 0.2 to 0.8 part per million of copper as due to the attainment of a critical thickness of the copper layer seems less plausible than the possibility that there is a critical concentration of copper in the acid below which copper reaches the specimen surface too slowly to prevent the formation of a protective film. Observations relating to the surface film formed in 7 percent acid containing 0.1 part per million of copper are presented in the following section.

An attempt to study the form of the copper on the surface of samples of II by electron diffraction was unsuccessful because exposure to 7 percent acid with 0.8 part per million of copper for several periods of time produced at most a few faint diffuse diffraction rings which were not sufficient for determining the surface phase. Since the diffraction spots and Kikuchi lines of aluminum were strong, any film of copper present must have been extremely thin.

It may be noted that the copper and iron impurities in the specimen cannot make a large contribution to the total impurity content of the acid since, even if a specimen of III were dissolved completely, the result would be only 0.1 part per million of copper and 1 part per million of iron in the acid. These impurities may conceivably contribute to the local corrosion process when their concentrations in the boundary are high.

Slow Intergranular Corrosion

Prior to the discovery of the difference between M and H water, a number of specimens of I, II, and III had been exposed to 7 percent acid made up with H water and thus containing only 0.1 part per million of copper. In none of these samples did intergranular corrosion progress more than 0.1 millimeter in several months. The behavior was different in a number of respects from that observed at high rates of intergranular attack. For one, bubble evolution was almost absent. In addition, the intergranular attack was not uniform but generally appeared as a string of small pits along the boundary as had been observed by Perryman; there was no attack of the grain surfaces except for fine pitting. There was also evidence that a protective surface film had been built up since samples exposed 43 days and then transferred without re-etching to 20 percent acid or to 7 percent acid containing 0.8 part per million of copper often remained unattacked for several days to more than a week. An examination by electron diffraction of a sample exposed 57 days indicated more surface phase than that observed in samples exposed in 20 percent acid or in 7 percent acid containing 0.8 part per million of copper. This sample exhibited a crystalline possibly oriented surface phase with interplanar spacings of 2.05 A (weak to moderate intensity), 1.39 A (very

weak), 1.18 A (weak to moderate), 1.07 A (weak), and 0.83 A (weak). This is thought to represent a hydroxide phase; it is not the usual amorphous product of oxidation in aqueous solution at room temperature nor is it thought to be alpha-alumina despite an unexpected correspondence of the spacings (not the relative intensities). It is uniformly thin and thus would not be attributable to a conversion product of the original thick gamma-alumina film (of which patches remain for several days at most after the preliminary etching treatment). For comparison, samples of I, II, and III exposed in 20 percent acid show only a single very weak diffraction ring corresponding to an interplanar spacing of approximately 2.03 A. The procedure for electron-diffraction samples was to plunge them in methanol, rinse thoroughly with methanol, and insert immediately into the camera (RCA Electron Microscope). There is no evidence of observable film formation due to this procedure since a specimen suffering rapid hydrogen evolution all over its surface, where there is no opportunity for a film to form in the solution, does not show the partial diffraction rings observed in the cases noted above.

After 65-day exposure, estimation of the depth of intergranular penetration microscopically by focusing on the surface and the bottom of the shallow V-grooves indicated some trend toward a greater rate of intergranular attack the lower the final annealing temperature and the higher the iron content. Samples quenched from 647° C were sectioned, and the maximum penetration was found to be about 20 microns in I and II and about 60 microns in III. That the penetration is the same for I and II is not inconsistent with the observations of Perryman under apparently similar conditions of corrosion since he studied mainly materials of iron content higher than that of II. However, the small and erratic differences between I and II observed by focusing or sectioning suggest that slow intergranular attack would occur in this acid even in the absence of impurities in the aluminum. The data are in agreement with those of Perryman in suggesting that sufficiently high concentrations of iron (and possibly other impurity) atoms in the boundaries increase the rate of intergranular attack. This is an additional feature in which the intergranular corrosion differs at low rates of attack from that formerly observed in acid compositions where the rate was high.

DISCUSSION OF STRUCTURE AND SUSCEPTIBILITY OF GRAIN BOUNDARIES

At the boundary between adjoining grains of different orientation, the crystal lattices cannot in general be in register and there must be a region where the atomic positions form the transition from one lattice to the other. The transition region is considered to consist of a central portion of irregular structure but not amorphous, perhaps three atom planes in thickness, where the atoms have definite positions although not those of either lattice, together with outer portions where

the lattice of each grain is normal but is acted on by stresses which
vanish at small distances from the center of the boundary. The grain
"boundary" is thus a region. Many of its features are believed to be
indicated in the bubble-raft models of Bragg and Nye (ref. 15).

Associated with the boundary is an "interfacial" free energy which
gives rise to phenomena analogous to those produced by the interfacial
tension between two liquids and which has in some cases been measured.
Structurally, this free energy is the result of the lattice disturbances
in the transition region; it is distributed throughout this region in
addition to the free energy the same amount of material would have if
there were no boundary. If the excess free energy of the transition
region can appear as chemical energy in a corrosive medium, this region
will be anodic to the body of the grain.

The interfacial free energy has been determined for copper as
550 ergs per square centimeter at about 900° C, for gamma-iron as 850 ergs
per square centimeter at 1,105° C (ref. 16), and also for gold as 365 ergs
per square centimeter at 1,027° C (ref. 17). At room temperature, the
interfacial energies will be higher because the entropy term is then
smaller for several reasons. A value of 500 ergs per square centimeter
is taken as a working estimate for a general grain boundary of aluminum
at room temperature. It has been shown that, excluding low-angle bound-
aries, the interfacial energy in aluminum does not vary greatly with
orientation difference except near a twin orientation or in certain cases
when the boundary is near a plane of symmetry (ref. 18).

If the excess free energy in the transition region is taken to lie
principally in a region several atomic planes in thickness, say 8 A, the
free-energy difference per unit volume for the general grain boundary is
6,300 joules per gram-molecule. For aluminum dissolving at hypothetical
reversible electrodes, from the relation $\Delta G = -nF\epsilon$ where ΔG is the
excess free energy per unit volume of the boundary, ϵ is the difference
between the potentials of the grain-boundary and grain-body electrodes,
and nF is the quantity of electricity corresponding to the dissolution
of one gram-molecule of metal, the boundary would be 22-millivolts anodic.
This is sufficient to make the metal potentially susceptible to inter-
granular corrosion. Further, the excess free energy per atom is not the
same for all atoms in the boundary, and some will be substantially more
active than the calculated average potential difference would imply.

Even in the nonreversible case of actual corrosion, the grain bound-
ary will still be anodic because of its higher (more positive) free energy.
Depending on the surface conditions in the corrodent, the difference in
solution potentials may be reduced to a very low value, but there is no
reason to believe that the boundaries can be made cathodic (except per-
haps under very special conditions as in the presence of considerable
copper in the test solution in the case described above). Thus the

conclusion from the experimental work that the grain boundaries of ideally pure aluminum would be significantly anodic is a reasonable one from these considerations of the boundary energy. Moreover, any ideally pure metal should be susceptible to intergranular corrosion when polarization of the corrosion reaction does not prevent the attack from progressing. That aluminum in hydrochloric acid is an apparently isolated instance of rapid intergranular disintegration in a "pure" metal is merely to be ascribed to the particular mechanism of corrosion which permits intergranular attack to continue at a substantial rate.

It may be argued that the free energy of the additional surface exposed by intergranular corrosion more than counterbalances the inter-facial energy so that intergranular corrosion would be energetically unfavorable as compared with ideally uniform surface corrosion where no increase in the surface area or energy is involved. However, even for an aluminum single crystal in hydrochloric acid, corrosion of the surface by the removal of layers which are uniform on an atomic scale does not occur; surface corrosion as well as intergranular corrosion increases the surface area of the specimen and, this factor being similar for both cases, intergranular corrosion is favored because of the higher free energy of the grain boundary.

The reduction of the rate of intergranular attack in 20 percent hydro-chloric acid by the segregation of iron and possibly other impurity atoms in the boundaries may be due to one or several factors. Either their presence has lowered the local energy (effect common to all elements which segregate) or it is a shift in the solution potential of the grain-boundary region due to its increased alloy content which is involved (effect spe-cific to the element). Although only a fraction of the sites in the bound-ary can be occupied by solute atoms, the lowering of the local energy at the most active sites might be a significant factor in reducing the sus-ceptibility of the boundary to corrosion. In the case of iron, increased alloy content makes the solid solution cathodic in hydrochloric acid so that segregated iron atoms act to reduce the rate of attack both through their effect on the local energy and their effect in making the boundary region less anodic, and, therefore, with iron, no clue is provided as to which of these effects is more important.

In the case of slow intergranular attack in 7 percent acid with 0.1 part per million of copper, sufficiently high grain-boundary concen-trations of iron and possibly other impurity atoms have the opposite effect; that is, they increase the rate of attack. The difference in behavior may be related to the more substantial surface film formed in this acid, but the data available for this case are too limited for fur-ther discussion. However, it may be noted with regard to the suggestion that slow intergranular attack would occur in this acid even in the absence of impurities in the aluminum that this is to be expected if the boundaries are inherently anodic. The presence of a thin film might

K

reduce the rate of the cathode or the anode reaction but would not be
expected to alter the anodic character of the boundary, so that inter-
granular attack of ideally pure aluminum should be observable in this
acid if the film is thin enough for the rate to be appreciable.

.CONCLUSIONS

The conclusions of the present investigation may be summarized as
follows for rapid intergranular corrosion of high-purity aluminum in
hydrochloric acid (i.e., in 20 percent acid with 0.1 part per million of
copper or 7 percent acid with about 0.8 part per million of copper):

1. Iron (and possibly other impurity) atoms have a strong tendency
to segregate at sites in the grain boundary. This segregation reduces
the rate of intergranular attack.

2. The grain boundaries are anodic inherently, that is, in the
absence of impurities. This is concluded to be a reasonable consequence
of the greater free energy per unit volume in the grain-boundary region
because of the contribution of the interfacial free energy.

3. Rapid intergranular attack occurs under conditions where there
is a local action producing a continual evolution of hydrogen gas from
the intergranular crevice. For rapid and selective attack, the strength
and metallic impurity content of the hydrochloric acid must be just below
the levels which result in continual hydrogen evolution over the entire
specimen.

4. In the materials studied, the particles of the aluminum-iron
second phase observed after certain heat treatments were not sufficiently
numerous to have a substantial influence on intergranular corrosion. It
was necessary to postulate that intergranular corrosion can be influenced
by impurity-concentration gradients in the solid solution associated with
boundaries. To such gradients was attributed the rapid attack of sub-
grain and low-angle grain boundaries (which normally are attacked slowly)
observed after certain heat treatments on exposure to solutions of rela-
tively low acid strength and high copper content.

5. Preferential corrosion of the grain body was found only in some
areas of specimens with relatively inactive grain boundaries and was due
to the manner in which copper in the acid cemented out on the specimen
surface rather than to the distribution of impurities in the specimen.

When the strength and metallic-impurity content of the acid are
low (tests in 7 percent acid with 0.1 part per million of copper), inter-
granular attack is slow and different conditions prevail. There is no

continual evolution of hydrogen gas, the surface film is thicker, and the intergranular attack is increased by sufficiently high concentrations of iron and possibly other impurity atoms in the boundaries.

Columbia University,
     New York 27, N. Y., June 25, 1953.

REFERENCES

L. Mears, R. B., and Brown, R. H.: Causes of Corrosion Currents. Ind. and Eng. Chem., vol. 33, no. 8, Aug. 1941, pp. 1001-1010.

2. McLean, D.: Discussion, Jour. Inst. Metals, vol. 73, 1947, pp. 791-793.

3. Cottrell, A. H.: Effect of Solute Atoms on the Behaviour of Dislocations. Conf. on Strength of Solids, Phys. Soc. (London), 1948, pp. 30-38.

4. Thompson, D. H., and Tracy, A. W.: Influence of Composition on the Stress-Corrosion Cracking of Some Copper-Base Alloys. Jour. Metals, vol. I, no. 2, Feb. 1949, pp. 100-109.

5. Rohrman, F. A.: The Effect of Heat Treatment on the Corrosion of High Purity Aluminum. Trans. Electrochem. Soc., vol. 66, 1934, pp. 229-237.

6. Lacombe, P., and Yannaquis, N.: La Corrosion intercrystalline de l'aluminium de haute pureté. Rev. Métallurgie, t. 45, fasc. 3-4, Mar-Apr. 1948, pp. 68-77.

7. Roald, B., and Streicher, M. A.: Corrosion Rate and Etch Structures of Aluminum; Effect of Heat Treatment and Impurities. Jour. Electrochem. Soc., vol. 97, no. 9, Sept. 1950, pp. 283-289.

8. Mears, R. B., Brown, R. H., and Dix, E. H., Jr.: A Generalized Theory of the Stress Corrosion of Alloys. Symposium on Stress-Corrosion Cracking of Metals, A.S.T.M. and Am. Inst. Min. and Metall. Eng., 1944, pp. 323-339.

9. Chaudron, G., Lacombe, P., and Yannaquis, N.: Intergranular Corrosion of Pure Aluminum in Relation to the Behaviour of Grain-Boundaries During Melting. Nature, vol. 162, no. 4126, Nov. 27, 1948, pp. 854-855.

10. Edgar, J. K.: Solubility of Iron in Solid Aluminum. Trans. Am. Inst. Min. and Metall. Eng., vol. 180, 1949, pp. 225-229.

11. Kê, T'ing Sui: Experimental Evidence of the Viscous Behaviour of Grain Boundaries in Metals. Phys. Rev., vol. 71, no. 8, Apr. 15, 1947, pp. 533-546.

12. Lacombe, P., and Berghezan, A.: Mise en évidence d'imperfections
    de structure de gros cristawx de solution solide Al-Zn all cours
    de leur durcissement structural. Comp. rend., Acad. Sci. (Paris),
    t. 226, June 28, 1948, pp. 2152-2154.

13. Randall, M., and Young, L. E.: The Calomel and Silver Chloride
    Electrodes in Acid and Neutral Solutions. The Activity Coefficient
    of Aqueous Hydrochloric Acid and the Single Potential of the Deci-
    Molal Calomel Electrode. Jour. Am. Chem. Soc., vol. 50, no. 4,
    Apr. 1928, pp. 989-1004.

14. Edeleanu, C., and Evans, U. R.: The Causes of Localized Character
    of Corrosion on Aluminium. Trans. Faraday Soc., vol. XLVII,
    pt. 10, no. 346, Oct. 1951, pp. 1121-1135.

15. Bragg, W. L., and Nye, J. F.: A Dynamical Model of a Crystal
    Structure. Proc. Roy. Soc. (London), ser. A, vol. 190, no. 1023,
    Sept. 9, 1947, pp. 474-481.

16. Fisher, J. C., and Dunn, C. G.: Imperfections in Nearly Perfect
    Crystals. John Wiley & Sons, Inc., 1952, pp. 317-351.

17. Buttner, F. H., Udin, H., and Wulff, J.: Determination of the
    Absolute Grain Boundary Energy of Cold at 1300° K. Jour. Metals,
    vol. 5, no. 2, 1953, pp. 313-317.

18. Friedel, J., Cullity, B. D., and Crussard, C.: Étude de la tension
    capillaire d'un joint dano un métal en fonction de l'orientation
    des grains qu':1 sépare. Acta. Mettallurgica, t. 1, fasc. 1,
    Jan. 1953, pp. 79-92.

TABLE I

SOLID SOLUBILITY OF IRON IN HIGH-PURITY ALUMINUM

Temperature, $^{\circ}$C	655	640	600	550	500	450	400	300
Iron, weight percent . . .	0.052	[a]0.043	[a]0.025	[a]0.013	[a]0.006	[b]0.002	[b]0.0008	[b]0.00006

[a]Experimental values of Edgar (ref. 10).

[b]Obtained by extrapolation.

TABLE II

CHEMICAL ANALYSES OF HIGH-PURITY ALUMINUM SHEET

[Analyses furnished by Aluminum Company of America]

Designation	Thickness, in.	Composition, weight percent						
		Fe	Cu	Si	Mg	Mn	Na	Ca
C	0.040	0.006	0.0032	0.0020	0.0006	--------	<0.0001	<0.0006
I	.064	.0004	.0022	.0006	.0004	<0.0002	.0001	<.0002
II	.064	.0039	.0022	.0007	<.0002	<.0002	.0001	<.0002
III	.064	.023	.0022	.0007	.0002	<.0002	.0001	<.0002

TABLE III

ANALYSES OF WATERS AND ACID

(a) Qualitative analyses of distilled waters from two stills

[Spectrographic estimates by Lucius Pitkin, Inc., on samples
    concentrated by evaporation in a polyethylene-silica system]

Designation	Composition, parts per million						
	Cu	Fe	Pb	Si	Mg	Al	Mo
M water (preliminary work)	1	0.1	0.01	3	0.03	0.01	----
H water (later work)	.1	[a]3	.03	3	.1	.01	0.03

[a]Contamination suspected during preparation of concentrate.
Other data suggest that this figure should be lower.

(b) Chemical analysis of one lot of chemically pure
concentrated hydrochloric acid

[Analysis furnished by W. C. Koch, General Chemical Division,
    Allied Chemical and Dye Corp.]

Composition, parts per million						
Heavy Metals (as Pb)	Fe	Nonvolatile	SO_4	Free Cl	SO_2	As
0.11	0.19	1	1.1	Nil	1	<0.005

TABLE IV

EFFECT OF RATE OF COOLING ON INTERGRANULAR CORROSION OF

HIGH-PURITY ALUMINUM IN 7 PERCENT HYDROCHLORIC ACID

CONTAINING ABOUT 0.8 PART PER MILLION OF COPPER

[Material C, 0.006 percent iron, heated 18 hr
at 600° C in evacuated Pyrex tubes]

Cooling medium	Failure time, days	Remarks (a)
Water quench (Annealed in air in an Alundum boat)	5	------------------------------
Water quench	7	------------------------------
Water quench followed by immersion in liquid nitrogen	6	------------------------------
Air blast[b]	5	Subgrain boundaries corroded through
Liquid nitrogen[b]	8	Subgrain boundaries corroded through
Oil at 30° C[b]	12	Subgrain boundaries attacked
Oil at 200° C[b]	12	Subgrain boundaries attacked; a little general corrosion
Furnace cool in 8 hr	15, 23	Some subgrain boundaries show shallow attack; some grain boundaries are sharply attacked, others weakly, others are in relief; general corrosion results in roughening of surface and thinning of specimen.
Furnace cool in 24 hr	19	

[a]All except furnace-cooled specimens show strong intergranular corrosion.

[b]Pyrex tube did not crack during quench.

TABLE V

EFFECT OF FINAL ANNEALING TEMPERATURE ON INTERGRANULAR

CORROSION RATE OF SINGLE-PHASE HIGH-PURITY

ALUMINUM IN 20 PERCENT HYDROCHLORIC ACID

Final annealing temperature before quenching, °C	Failure time, days, for specimens -		
	Heated directly	Quenched from 647° C, reheated	Furnace cooled from 647° C, held
Composition I, 0.0004 percent iron			
647 (24 hr)	4,4,5,5	----	--------
600 (48 hr)	6	----	--------
500 (96 hr)	13	7,12	--------
Composition II, 0.004 percent iron			
647	4,5,5,5,6,6	----	--------
600	7	----	9,9
550 (72 hr)	------------	9,16	11,13,13
Composition III, 0.023 percent iron			
647	11,13	----	--------

TABLE VI

EFFECT OF FINAL ANNEALING TEMPERATURE ON RATE OF INTERGRANULAR

CORROSION OF SINGLE-PHASE HIGH-PURITY ALUMINUM IN

7 PERCENT HYDROCHLORIC ACID CONTAINING

0.8 PART PER MILLION OF COPPER

[All samples heated 24 hr at 647° C; all samples thinned
slightly because of uniform general corrosion.]

Condition	Failure time, days, for -		
	Composition I	Composition II	Composition III
Water quench	4	4	(a)
Furnace cool to 605° C, hold 48 hr, water quench	6	7	---

[a]Intergranular attack slow; fails by general corrosion.

TABLE VII

EFFECT OF IRON CONTENT AND COOLING RATE ON INTERGRANULAR CORROSION

RATE OF HIGH-PURITY ALUMINUM IN 20 PERCENT HYDROCHLORIC ACID

[All samples heated 24 hr at 647° C]

Condition	Failure time, days, for -		
	Composition I, 0.0004 percent iron	Composition II, 0.004 percent iron	Composition III, 0.023 percent iron
Water quench	4-5	4-6	11,13
Liquid-nitrogen quench (sealed in Pyrex tube)	6	5	8
Furnace cool at 75° C/hr	9	8	2 (pitting)
Furnace cool at 4.5° C/hr	8	9	1 (pitting

TABLE VIII

EFFECT OF COMPOSITION OF HYDROCHLORIC ACID ON RATE OF INTERGRANULAR

CORROSION OF SINGLE-PHASE HIGH-PURITY ALUMINUM

(a) Composition C (0.006 percent iron, 0.040-in. thick,
annealed at 600° C for 18 hr, water quenched)

Percent HCl by weight	Major metallic impurity in acid, part per million	Failure time, days	Remarks (a)

7	0.1 Cu
	About .8 Cu
	. .8 Cu
	
	8 Fe
		>100
		4
		4
		
		15
			H water
			M water
			Cu added to
			  H water
			Fe added to
			  H water

7 16 20 25	0.1 Cu	>100 37 4 1$\frac{1}{2}$	---------------- ---------------- ---------------- Some uniform GC

(b) Composition I (0.0004 percent iron, 0.064-in thick, annealed at
647° C for 24 hr, water quenched; CuCl$_2$ or FeCl$_3$ added
to H water)

Percent HCl by weight	Major metallic impurity in acid, part per million	Failure time, days	Remarks (a)
7	0.1 Cu .2 Cu .8 Cu 8 Cu	>>63 >65 4,6 --------	---------------- ---------------- Some GC Rapid uniform GC only
20	0.1 Cu .8 Cu 1 Fe 10 Fe	4,5 2 2$\frac{1}{2}$ 2	---------------- Considerable nonuniform GC ---------------- ----------------

[a]GC, general corrosion. GC noted above is that observed at the
time when only a few grain boundaries had been corroded through.

L-85626

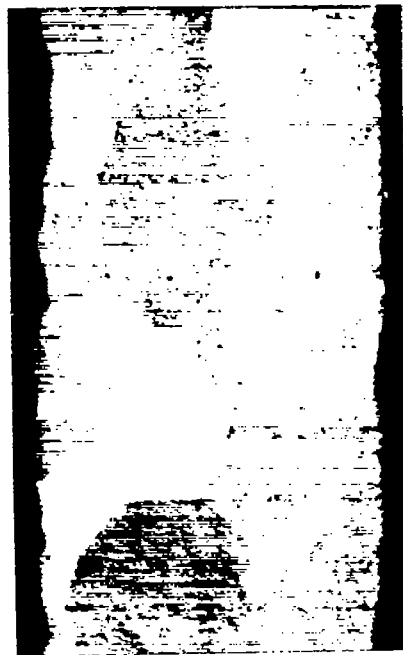(a) As quenched.   (b) Reheated at 400° C
                                        for 4 hours.

Figure 1.- Effect of reheating on attack of low-angle grain and subgrain
    boundaries after 6 days in 7 percent hydrochloric acid containing
    0.8 parts per million of copper. Aluminum C, 0.006 percent iron,
    annealed at 600° C for 18 hours, and water quenched. 6X.

(a) Aluminum I, 0.0004 percent   (b) Aluminum III, 0.023 percent
            iron.   iron.

L-85627

Figure 2.- Effect of iron content on intergranular attack after 16 days
    in 20 percent hydrochloric acid. Specimens quenched from 647° C.   6X.

L-85628

Figure 3.- Grain boundaries in relief in one area of specimen.
Aluminum III, quenched from 647° C and exposed 5 days to 7 percent
hydrochloric acid containing 0.8 part per million of copper. Oblique
illumination; 6X.

L-85629

Figure 4.- Intergranular attack on a slow-cooled specimen. Aluminum III,
cooled from 647° C at 4.5° C per hour and exposed 1 day to 20 percent
hydrochloric acid. 6X.